HIGH TEMPERATURE STUDY OF ANHARMONIC PROPERTIES OF LANTHANUM SULPHIDE CRYSTAL

Chandan Gupta[1]*, Kailash[2] and Jitendra Kumar[3]

[1]Department of Physics, Bundelkhand University, Jhansi, U.P, 284128, India.
[2]Department of Physics, BNV PG College, Rath, Hamirpur, U.P, 210431, India.
[3]Department of Physics, Govt. Girls P.G. College, Banda, U.P. 210001, India.

* *Corresponding Author Email: chandanphysics84@gmail.com*

"together we can and we will make a difference"

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[1]Department of Physics, Bundelkhand University, Jhansi, U.P, 284128, India.
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[3]Department of Physics, Govt. Girls P.G. College, Banda, U.P. 210001,India.

Email: chandanphysics84@gmail.com, kailash.rath@yahoo.co.in, jkumarsh@gmail.com

ABSTRACT

For the deformed face centered cubic crystal one can get the Taylor's series expansion of elastic energy density starting from nearest neighbor distance and hardness parameter utilizing Coulomb and Born Mayer potentials. The knowledge of the higher order elastic constants for a crystal can be used to obtain the anharmonic properties of the crystals by theoretical approach. The Lanthanum Sulphide crystal possesses face centered cubic crystal structure. The theory is developed for obtaining second, third and fourth order elastic constants of Lanthanum Sulphide single crystals up to an elevated temperature and higher order elastic constants of Lanthanum Sulphide single crystals at an elevated temperature are evaluated. The data thus obtained is used to evaluate the first order pressure derivatives of second and third orders elastic constants, second order pressure derivatives of second order elastic constants and partial contractions.

Keywords: *Higher order elastic constants, Hardness parameter, Anharmonic Properties.*

INTRODUCTION

In recent material science we need values of elastic constants at elevated temperatures. In the last few years studies of anharmonic properties of monovalent compounds have attracted the attention of the physicists since they provide much valuable information regarding crystal structure[1-3]. Many properties of crystlas are thermodynamically linked with specific heat, thermal expansion and Debye temperature and Grüneisen numbers. Many researchers evaluated the anharmonic properties, such as second, third and fourth order elastic constants (SOECs, TOECs and FOECs), first order pressure derivatives (FOPDs) of SOECs and TOECs, second order pressure derivatives (SOPDs) of SOECs of several ionic crystals. Third and fourth order elastic constant are essential to study a number of anharmonic properties of crystals[4-6]. The thermal contribution to elastic constants is very significant, the experimental data reveal that in going from 0 K to higher temperature, the values of second order elastic constants (SOECs) are changed considerably even for highly ionic solids like LaS[7-10]. No complete experimental or theoretical efforts have been made so for in obtaining the temperature variation of anharmonic properties of divalent materials possessing different crystal structures at an elevated temperature[11]. When the elastic energy density for a strain components; The SOECs, TOECs and FOECs deformed crystal is expanded as a power series of strains using Taylor's series expansion, the coefficients of the quadratic cubic and quartic terms are known as SOECs, TOECs and FOECs. A number of crystal anharmonicities like specific heat at higher temperature, thermal expansion, temperature dependence of acoustic velocities along different directions, acoustic attenuation, Grüneisen parameters are directly related to SOECs and TOECs[12-15]. The present paper is mainly focused on the study of temperature variation of higher order elastic constants and their pressure derivatives up to an elevated temperature for LaS using Born Mayer and coulomb potential starting from the nearest neighbor distance and hardness parameter. In the absence of any measured data on the elastic properties at higher temperature for this compound, comparison cannot be made.

Theory

The elastic energy density for a crystal of a cubic symmetry in deformed state can be expanded as[16]:

$U_0 = U_2 + U_3 + U_4$

$= [1/2!] \ C_{ijkl} \ \alpha_{ij} \ \alpha_{kl} + [1/3!] C_{ijklmn} \ \alpha_{ij} \ \alpha_{kl} \ \alpha_{mn} + [1/4!] C_{ijklmnpq} \ \alpha_{ij} \alpha_{kl} \alpha_{mn} \ \alpha_{pq}$ \hfill (1)

Where C_{ijkl}, C_{ijklmn} and $C_{ijklmnpq}$ are the SOECs, TOECs and FOECs in tonsorial form; α_{ij} are the Lagrangian are as bellow:

$C_{ijkl} = C_{IJ} = (\partial^2 U/\partial\alpha_{ij}\partial\alpha_{kl})_{\alpha=0}$,

$C_{ijklmn} = C_{IJK} = (\partial^3 U/\partial\alpha_{ij}\partial\alpha_{kl}\partial\alpha_{mn})_{\alpha=0}$

and $\quad C_{ijklmnpq} = C_{IJKL} = (\partial^4 U/\partial\alpha_{ij}\partial\alpha_{kl}\partial\alpha_{mn}\partial\alpha_{pq})_{\alpha=0}$

C_{IJ}, C_{IJK} and C_{IJKL} are the SOECs, TOECs and FOECs in Brügger's definition and voigt notations.

At a temperature T the free energy density of a crystal is expressed as:

$$U_{Total} = U_0 + U^{vib} ,$$

where

$$U^{vib} = \frac{KT}{NV_c}\sum_{i=1}^{3sN}\ln 2 Sinh\left(\frac{\hbar\omega_i}{KT}\right)$$

(2)

U_0 is the internal energy per unit volume of the crystal when all ions are at rest on their lattice point positions, U^{vib} is the vibrational free energy of the crystal. V_c is the volume of the primitive cell, N is the number of the primitive cells in the crystal and s is the number of ions in the elementary cell. Other notations used in this equation have their usual meanings.

An elastic constant consists of two parts as follows:

$C_{IJ} = C_{IJ}^0 + C_{IJK}^{vib}$, $C_{IJK} = C_{IJK}^0 + C_{IJK}^{vib}$, $C_{IJKL} = C_{IJKL}^0 + C_{IJKL}^{vib}$

(3)

The first part is the strain derivative of internal energy U_0 and is known as static part and the second part is the strain derivative of the vibrational free energy U^{vib} and is called vibrational part.

This formulations are designed in C++ computer language. With the help of all these programs, we have calculated the various elastic constants and their pressure derivatives for Lanthanum Sulphide Crystal.

Evaluation

The theory for the calculation of different anharmonic properties of the substances possessing FCC crystal structures is given in the preceding section. The TOECs for LaS is evaluated from 300K to an elevated temperature (near melting point).

Throughout this temperature range LaS exhibits FCC crystal structure. Selecting a few data obtained in this study, the values of TOECs at room temperature are given in Tables 2. The FOPDs of TOECs have been evaluated utilizing data of TOECs and SOECs and the results are shown in Table 3. The whole evaluation is based on the assumption that the FCC crystal structure of the material does not change when temperature varies up to their melting point. The value of r_0 and q are taken as 2.8116×10^{-8} cm and 0.345×10^{-8} cm.

RESULTS AND DISCUSSION

One can observed from table 1 that the C_{11} is larger than other Second order elastic constants at room temperature. Among the calculated third order elastic constants of this material, C_{456} is largest in their absolute values and an order of magnitude larger than the SOECs. Magnitude of other C_{ijk}'s are smaller than those of C_{456}. For LaS, the values of C_{111}, C_{123}, C_{144}, C_{166} and C_{456} are positive in nature, while C_{112} is negative in nature at room temperature and shows a linear relationship with temperature variation. Among the calculated fourth order elastic constants for LaS in Table 2, C_{1111} is the largest in their values at room temperature. Magnitudes of other C_{ijkl}'s are smaller than those of C_{1111}. The values of C_{1111}, C_{1112}, C_{4444}, C_{1155} and C_{1266} are positive in nature, while C_{1123}, C_{1144}, C_{4455} and C_{1255} are negative in nature and also verify linear relationship with temperature variation. There are three first order pressure derivatives of second order elastic constants and six first order pressure derivatives of third order elastic constants are presented in Table 3. Among the calculated first order pressure derivatives of third order elastic constants for LaS dC_{111}/dP is larger than other ones. The values of dC_{123}/dP, dC_{144}/dP and dC_{456}/dP are positive in nature, while dC_{111}/dP, dC_{112}/dP and dC_{166}/dP are negative in nature at room temperature. The second order pressure derivatives of second order elastic constants and the values various partial contractions are shown in table 4. All the variations discussed above are represented graphically in Figs 1-10.

**Table 1 -** The SOECs and TOECs of LaS in 10^{11} dyne/cm^2

Temp(K)	C_{11}	C_{12}	C_{44}	C_{111}	C_{112}	C_{123}	C_{144}	C_{166}	C_{456}
300	17.01	6.20	6.34	-229.05	0.11	10.83	10.38	9.95	10.01
400	17.61	6.16	6.35	-227.68	-2.57	11.10	10.50	10.01	10.01
500	18.21	6.12	6.36	-226.34	-5.34	11.38	10.62	10.08	10.01
700	19.43	6.04	6.37	-223.68	-11.01	11.92	10.86	10.21	10.01
1000	21.27	5.92	6.39	-219.73	-19.61	12.74	11.22	10.40	10.01

Table 2 - The FOECs of LaS in 10^{12} dyne/cm^2

Temp(K)	C_{1111}	C_{1112}	C_{1122}	C_{1123}	C_{1144}	C_{1456}	C_{4444}	C_{1155}	C_{4455}	C_{1255}	C_{1266}
300	253.59	0.87	9.36	-2.39	-2.64	-2.34	14.11	11.76	-2.35	-2.61	13.81
400	233.02	-2.99	7.72	-2.41	-2.74	-2.34	14.07	11.51	-2.35	-2.71	13.66
500	212.47	-6.87	6.09	-2.43	-2.84	-2.34	14.02	11.26	-2.35	-2.80	13.51
700	171.36	-17.62	2.82	-2.46	-3.04	-2.34	13.93	10.77	-2.36	-2.98	13.21
1000	109.72	-26.25	-2.06	-2.46	-3.34	-2.34	13.79	10.52	-2.37	-3.26	12.76

Table 3 - The FOPDs of SOECs and TOECs of LaS (Dimensionless)

Temp(K)	dC_{11}/dP	dC_{12}/dP	dC_{44}/dP	dC_{111}/dP	dC_{112}/dP	dC_{123}/dP	dC_{144}/dP	dC_{166}/dP	dC_{456}/dP
300	-6.20	-1.00	-2.24	-60.41	-3.67	2.33	0.61	-2.23	2.36
400	-6.10	-0.81	-2.23	-50.01	-1.51	2.30	0.67	-2.04	2.34
500	-6.00	-0.62	-2.21	-39.93	0.58	2.27	0.72	-1.76	2.31
700	-5.82	-0.25	-2.19	-20.79	4.57	2.21	0.82	-1.49	2.27
1000	-5.58	0.26	-2.16	5.30	10.09	2.13	0.96	-0.99	2.21

Table 4 - The SOPDs of SOECs in 10^{-12} cm^2/dyne and Partial Contraction in 10^{13} dyne/cm^2
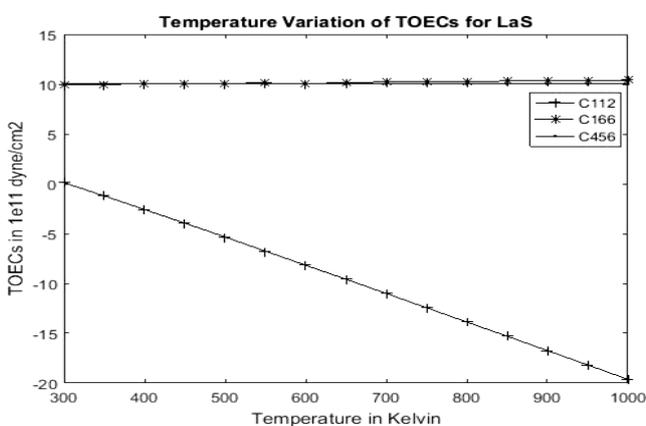
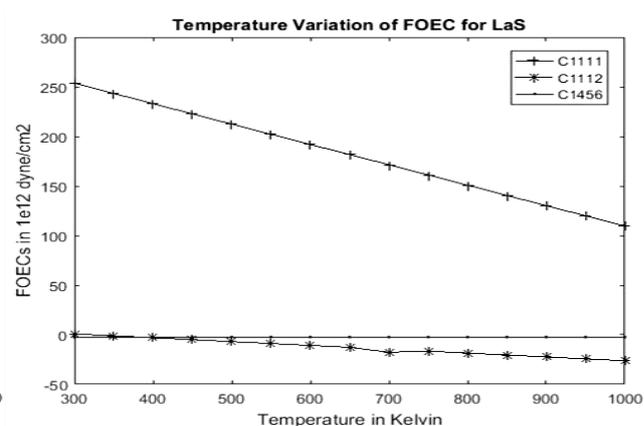| Temp(K)	d^2C_{11}/dP^2	d^2C_{12}/dP^2	d^2C_{44}/dP^2	Y_{11}	Y_{12}	Y_{44}
300	55.49	-1.45	-0.11	27.10	0.84	3.80
400	51.83	-1.32	-0.66	23.16	-0.26	3.67
500	48.48	-1.07	-1.19	19.22	-1.37	3.55
700	42.48	-0.29	-2.14	11.35	-3.59	3.29
1000	34.84	1.41	-3.31	-0.44	-4.70	2.91
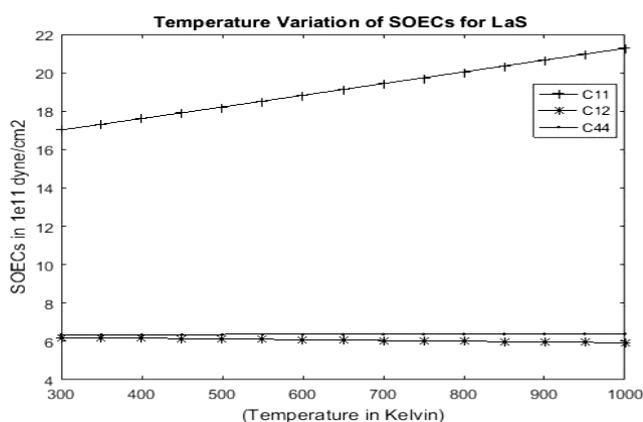
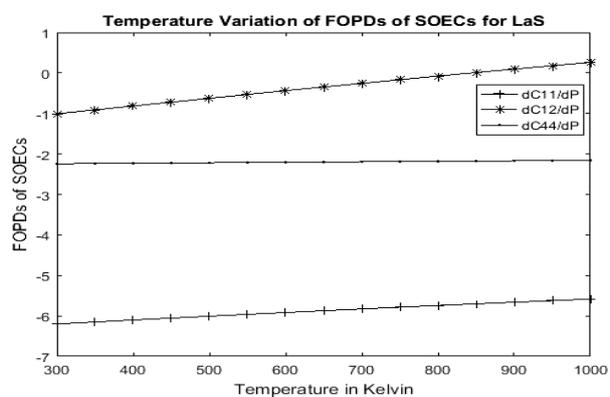

Fig. 1
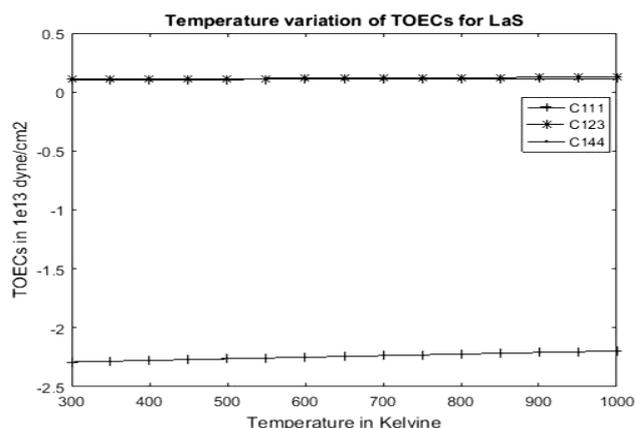
Fig. 2

Fig.3

Fig. 4
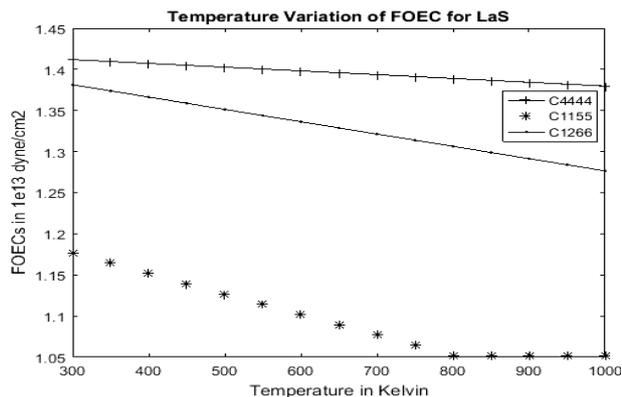
Fig.5
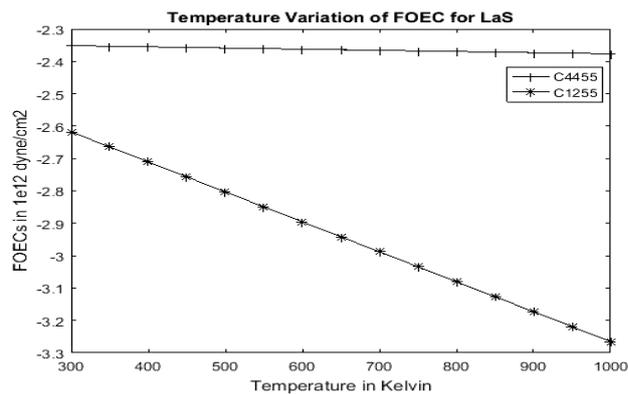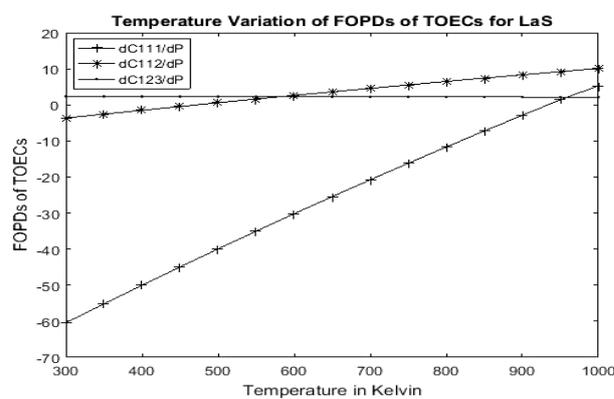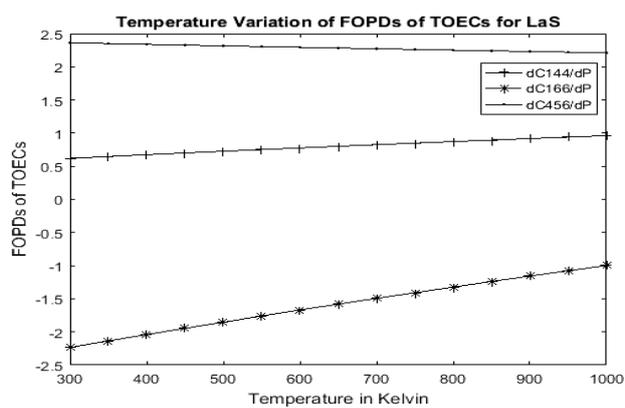

Fig. 6

Fig.7

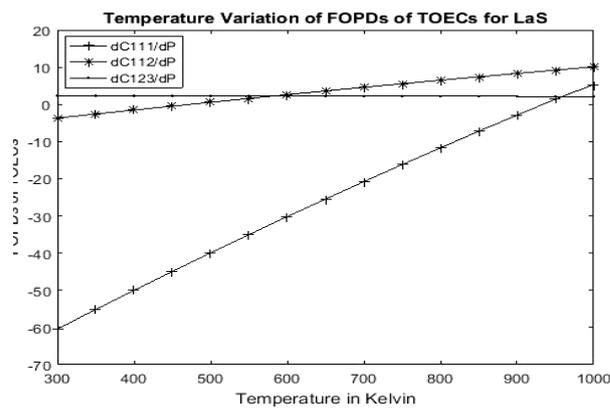**Fig. 8**

Fig.9

Fig. 10

CONCLUSIONS

The present study shows the validity of the theoretical approach and one can say that a very little variation of pressure derivatives of higher order elastic constant over temperature shows that the crystal can be used for acoustic purposes where high pressure and temperature is required. Since high temperature study is not possible experimentally, the present theoretical approach will behelpful to study these types of crystals at elevated temperatures. This theoretical approach has been successfully applied for mono-valant and di-valant crystals; also it can be used to study tri-valant crystals.

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